Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Elucidating the Conformational Energetics of Glucose and Cellobiose in Ionic Liquids

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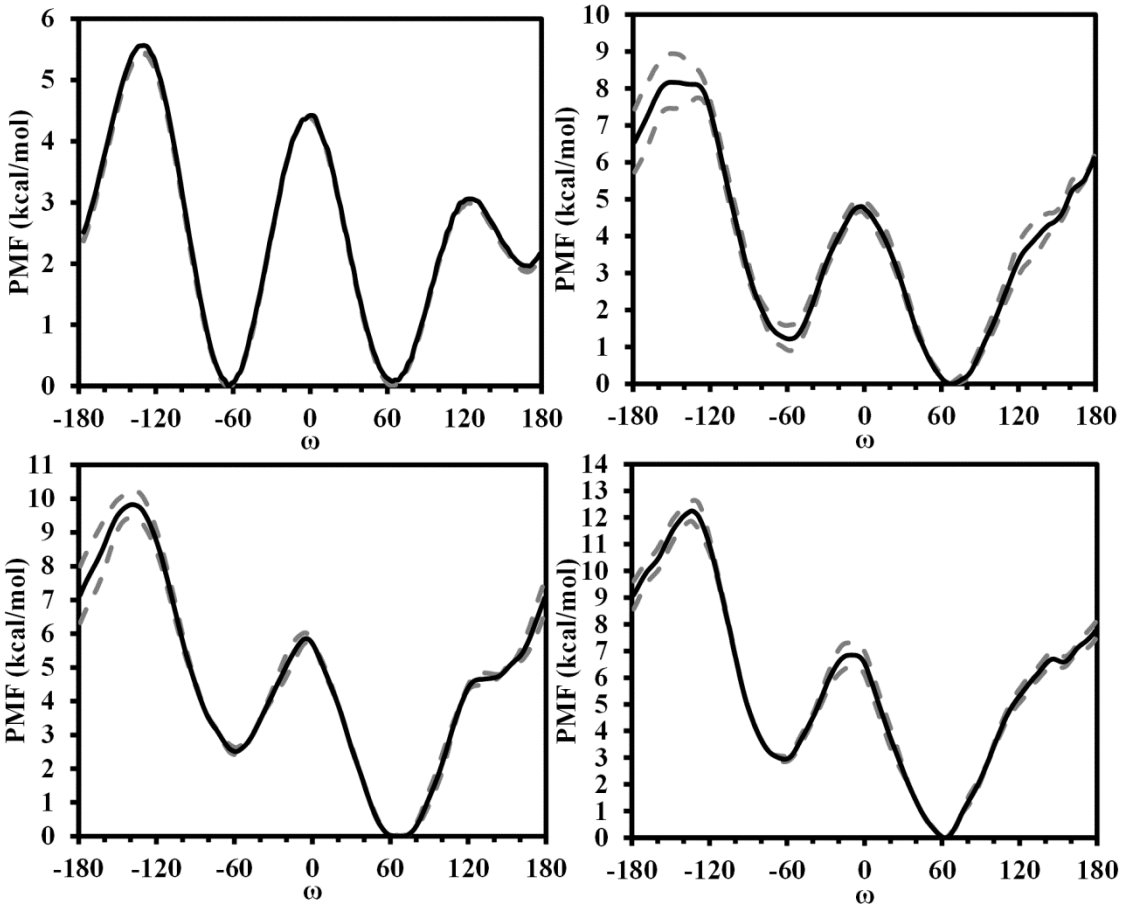

Figure S1 Convergence of the PMFs for the ω dihedral (O6-C6-C5-O5) of glucose in water (top left), EMIM OAc (Top Right), BMIM OAc (Bottom Left) and OMIM OAc (Bottom Right). The solid black line indicates the PMFs generated from the entire 8 ns while the dotted lines indicate PMFs generated from the first half and last half of the data. The resulting standard deviation is < 0.3 kcal/mole.

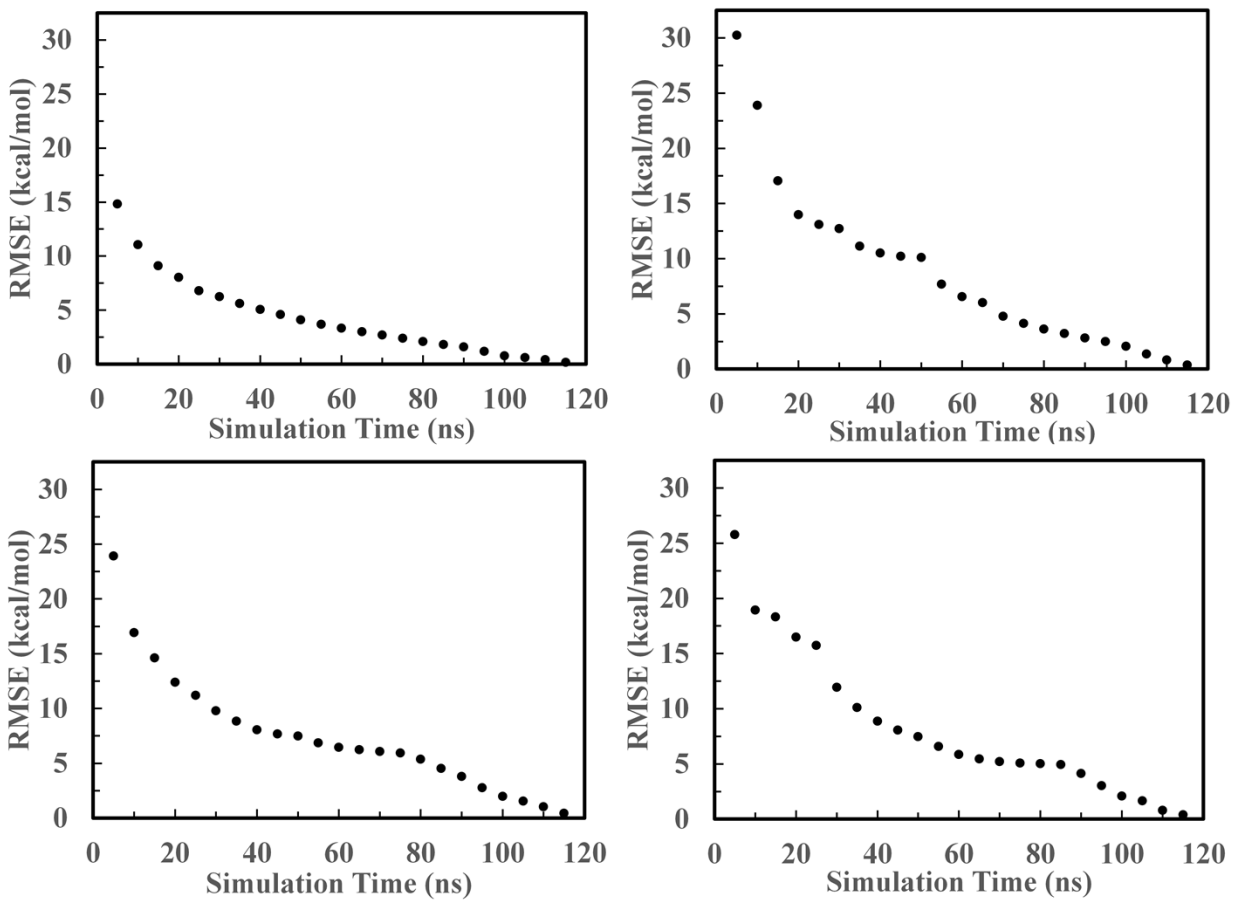

Figure S2: Convergence of the WTMD FESs demonstrated by calculating the Average Root Mean Square Errors (based on the 115 ns FES) for the points over the φ-ψ space for cellobiose in water (top left), EMIM OAc (Top Right), BMIM OAc (Bottom Left) and OMIM OAc (Bottom Right) with the 115 ns FES as the reference. The FESs are converged to within 1 kcal/mol for all 4 FESs.

Increase in Barrier at the TS with increasing cation alkyl chain length for the ω dihedral

From Figure 4 in the manuscript it is evident that the energy at the transition state also characteristically increases with increasing cation tail length. Figure S4 illustrates the volumetric occupancy maps at the transition state (TS) between the wells GG and GT at the ω ~0° configuration. The reason for the increasing trend in energy at the TS state is observed to be the imidazolium - ring oxygen interaction that results in unfavorable interactions of the alkyl tail with the hydroxymethyl group which progressively increases with increase in the alkyl tail length.

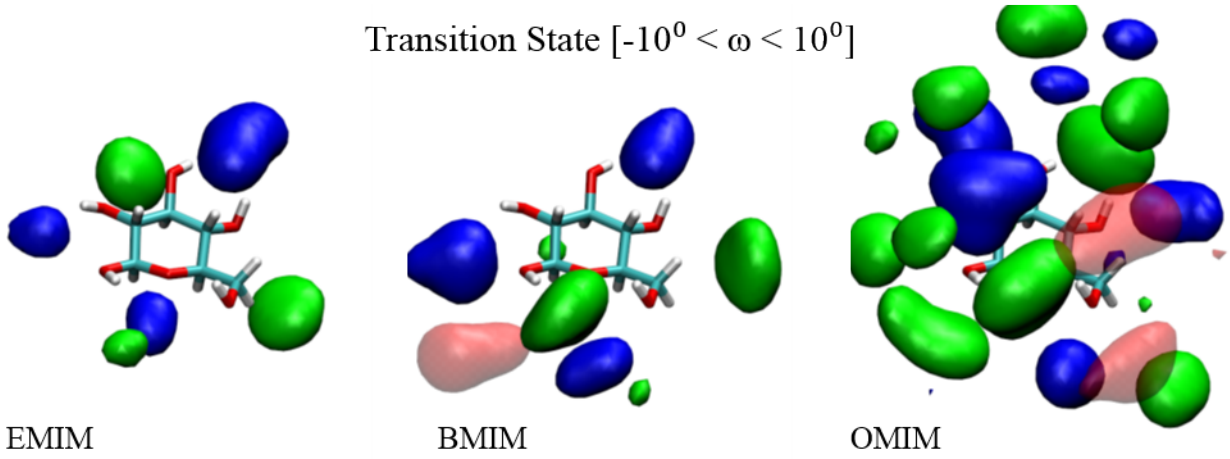

Figure S4: Volmap representation for acetates (Blue), Imidazolium ring (Green) and Cation Tail (Red Transparent) in TS (0°) for EMIM OAc (left) BMIM OAc (center) and OMIM OAc (right).

Interactions of the Cellobiose Ring Oxygens with the Solvent

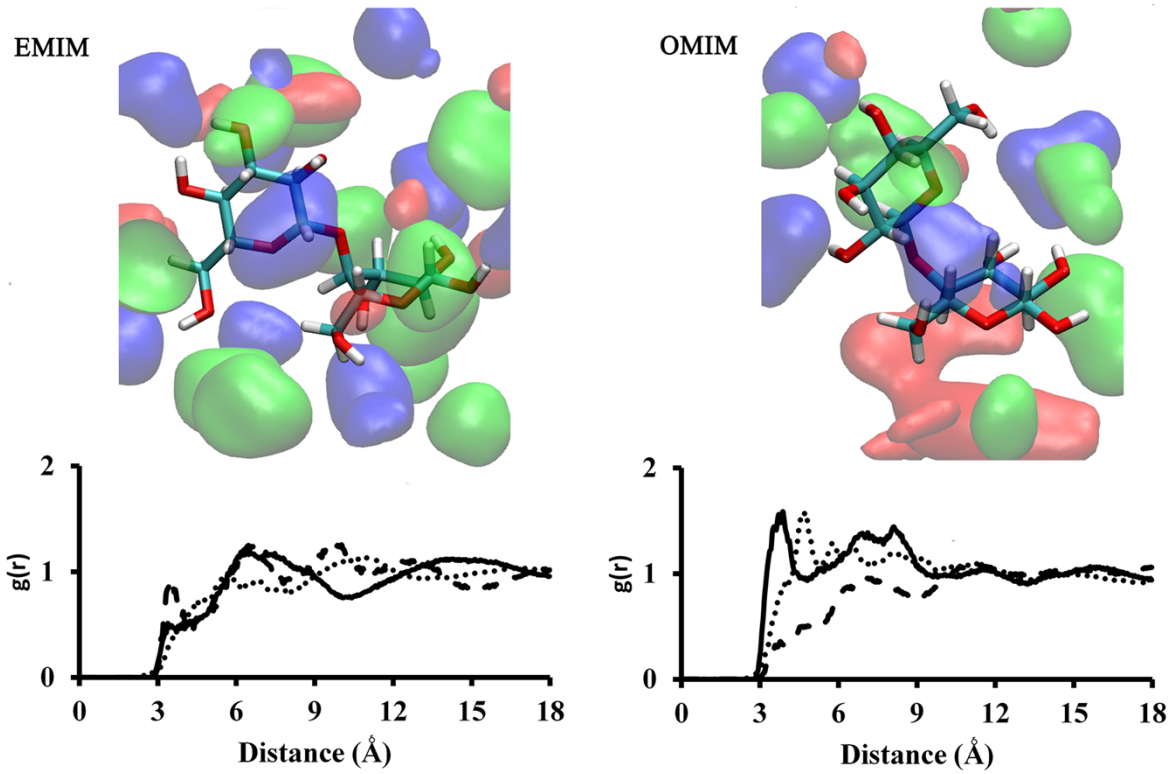

Figure S4 Iso-surface plots based on volumetric occupancy (Top) calculated from the conformations observed in the EMIM OAc (left) and OMIM OAc (Right) φ-ψ wells. The acetates are represented in transparent Blue, Imidazolium ring in transparent Green and Cation Tail in transparent Red. The interactions of the Ring Oxygens with the imidazolium ring (solid line), alkyl tail (dashed line) and the acetates (dotted line) indicated by RDFs (Bottom).

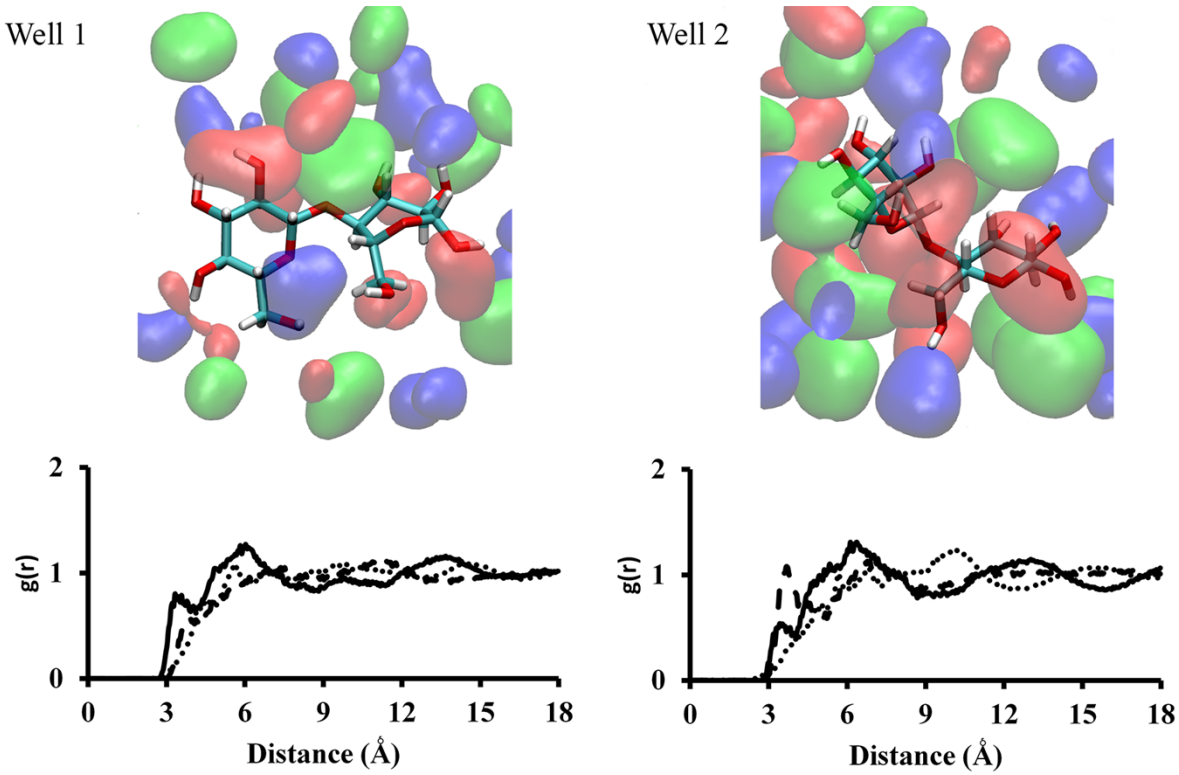

Figure S5 Iso-surface plots based on volumetric occupancy (Top) calculated from the conformations observed in the BMIM OAc Well 1 (left) and BMIM OAc Well 2 (Right). The acetates are represented in transparent Blue, Imidazolium ring in transparent Green and Cation Tail in transparent Red. The interactions of the Ring Oxygens with the imidazolium ring (solid line), alkyl tail (dashed line) and the acetates (dotted line) indicated by RDFs (Bottom).